Future Developments

As has been described above, there are many alternative approaches to the chromatographic analysis of commercial surfactants. The approach to be used for any analysis may be determined by a number of factors, the information required, the equipment available, the time available to carry out the analysis. As we move into the twenty-first century, there will be a trend towards faster analysis and analysis requiring less sample handling. Automation will increase, requiring less and less skilful human input. Data handling will become faster and more intelligent in order to deal with greater volumes of data generated in shorter times. Use of new separation techniques will be investigated, particularly electro-driven techniques and some will replace existing techniques for certain analyses. Overall, separation systems will become smaller with advantages of lower solvent and carrier gas use, less use of laboratory space, and with increased portability to permit use away from the laboratory.

See also: **II/Chromatography: Gas:** Detectors: Selective. **Chromatography: Liquid:** Derivatization; Detectors: Evaporative Light Scattering; Ion Pair Liquid Chromatography. **Chromatography: Thin-Layer (Planar):** Densitometry and Image Analysis; Layers. **III/Detergent Formulations: Ion Exchange. Surfactants:** Liquid Chromatography. **Thin-Layer Chromatography-Vibration Spectroscopy.**

Further Reading

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Liquid Chromatography

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Introduction

Liquid chromatography (LC) is very useful for the characterization of individual surfactants. Most commercial surfactants are mixtures of members of homologous series, and LC is capable of defining these mixtures according to their homologue distribution, indicating, for example, alkyl chain length or degree of polymerization. LC is also the preferred technique for the quantitative determination of many surfactants, especially ionic surfactants in mixtures. The utility of LC stems from the properties of surfactants – these compounds have good solubility in the usual LC mobile phases and possess diverse chemical functionality, but at the same time they are not volatile enough for ready analysis by alternative technologies such as gas chromatography (GC) or simple mass spectrometry (MS). The structures of common surfactants are given in **Table 1**.

Surfactants are usually analysed in LC systems containing a substantial percentage of organic solvent so as to inhibit micelle formation. The presence of micelles will confound LC analysis.

Formulations and Mixtures of Surfactants

LC is used for quality control of formulations such as cleaning compounds and pharmaceutical preparations. LC is often the easiest and most specific method for determining surfactant concentration in a well-understood mixture. On the other hand, LC is not often useful for analysis of unknown formulations unless MS detection is available. This is because of the limited separation range of any single LC system.

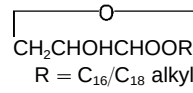
Sometimes, especially in quality control where there are no unknown components, no preliminary sample work-up is necessary. This is particularly true of ionic surfactants. More often, especially for nonionics, a gross separation of the surfactants from the matrix is required. This can be accomplished by solvent extraction of the dried solids or by liquid–liquid extraction or solid-phase extraction (SPE) of an aqueous solution.

Alkylarylsulfonates and alkylphenol ethoxylates can be determined with a minimum of sample work-up because of the availability of a specific detection method, fluorescence, to distinguish them from other surfactant and nonsurfactant compounds that may also be present. For the very common mixtures of anionic and nonionic surfactants, ion exchange chromatography systems result in nonionic surfactants eluting prior to anionics, while reversed-phase systems result in the nonionics being retained longer than anionics.

Environmental Analysis

LC is widely applied in environmental analysis, but it is not used for routine monitoring of effluents, except by industry for the analysis of specific process streams

Table 1 Structures of common surfactants

Surfactant	*Structure*
Cationic surfactants	
Quaternary amines	$RR'R''R'''N^+Cl^-$ R,R′,R″, R‴ = H or C_1–C_{18} alkyl or $C_6H_5CH_2$
Anionic surfactants	
Linear alkylbenzene sulfonates	4-$RC_6H_4SO_3^-Na^+$ R = $C_{10}H_{21}$–$C_{14}H_{29}$
Alkyl sulfates	$ROSO_3^-Na^+$ R = C_8H_{17}–$C_{18}H_{37}$
Alkanesulfonates	$RSO_3^-Na^+$ R = C_8H_{17}–$C_{18}H_{37}$
Ether sulfates	4-$RC_6H_4O(CH_2CH_2O)_xSO_3^-Na^+$ or $R'O(CH_2CH_2O)_xSO_3^-Na^+$ R = C_9H_{19}; R′ = $C_{12}H_{25}$–$C_{18}H_{37}$; x = 2–10
α-Olefin sulfonates (mixtures of alkenesulfonates and hydroxyalkanesulfonates)	$RSO_3^-Na^+$ R = $C_{11}H_{21}$–$C_{20}H_{39}$ or $C_{11}H_{22}OH$–$C_{18}H_{36}OH$
Ether carboxylates	$RO(CH_2CH_2O)_xCH_2COO^-Na^+$ R = $C_{12}H_{25}$–$C_{18}H_{37}$; x = 5–25
Sulfosuccinate esters	$ROOCCHSO_3CH_2COOR^-Na^+$ or $HOOCCHSO_3CH_2COOR^-Na^+$ R = C_8H_{17}
α-Sulfofatty acid methyl esters	$RCH(SO_3^-)COOCH_3Na^+$ and $RCH(SO_3^-)COO^-2Na^+$ R = $C_{12}H_{25}$–$C_{16}H_{33}$
Nonionic surfactants	
Alkylphenol ethoxylates	4-$RC_6H_4O(CH_2CH_2O)_xH$ R = C_8H_{17}, C_9H_{19} or $C_{12}H_{25}$; x = 3–50
Alcohol ethoxylates	$RO(CH_2CH_2O)_xH$ R = $C_{12}H_{25}$–$C_{18}H_{37}$; x = 5–60
Acid ethoxylates	$RCOO(CH_2CH_2O)_xH$ R = $C_{11}H_{23}$–$C_{17}H_{35}$; x = 5–20
EO/PO copolymers	$HO(CH_2CH_2O)_y(CH(CH_3)CH_2O)_x(CH_2CH_2O)_yH$ x = 16–70; y = 1–100
Esters	 R = C_{16}/C_{18} alkyl

where the composition is uniform and well understood. The standard wastewater methods, for example those based on colorimetric tests, give a gross value for total surfactant concentration and are most suitable for routine environmental monitoring.

LC is used, however, in special investigations of environmental impact to give information on the concentration and degradability of specific surfactants in particular environmental areas, relying on the ability of LC methods to precisely characterize surfactant homologues. A preliminary separation or preconcentration is always necessary. The most common pretreatment method nowadays is SPE, especially when low levels of surfactant must be determined. C_{18} media are most often applied, in the form of SPE cartridges or extraction discs. Nonpolar resin of the poly(styrene/divinylbenzene) type is also used. A secondary separation of the surfactants into nonionic, cationic and anionic fractions can be performed on ion exchange media.

LC is the method of choice for determining anionic surfactants in the environment. It is also preferred for the determination of the anionic degradation products of these surfactants. LC is the best method for the determination of nonionics (especially when coupled with MS), if detail on homologue distribution is needed. LC is less often applied to environmental determination of cationics, since interference is not as serious a problem with the standard methods for determining cationics in wastewater as it is for other surfactants.

Analysis of Individual Surfactants

Anionic Surfactants

LC analysis of anionic surfactants is a mature technology. Detection is a simple matter, either by direct UV absorption of aromatic surfactants or by inverse photometric detection of the aliphatic compounds.

Alkylarylsulfonates The commercial product, linear alkylbenzenesulfonate (LAS) is a mixture containing a range of alkyl chain lengths, typically C_{10}–C_{14}. Reversed-phase LC with a C_4 or C_8 column effectively separates LAS according to the length of the alkyl chain (**Figure 1**). A C_{18} packing gives a more complex chromatogram because the individual compounds of discrete alkyl chain length are themselves partially resolved into isomers; in many cases this resolution is not needed or desired (**Figure 2**). In any case, GC analysis after desulfonation is a better method for determining isomers. Aqueous mixtures of acetonitrile, methanol and tetrahydrofuran (THF) are appropriate mobile phases, generally containing a salt such as 0.1 mol L^{-1} sodium perchlorate. Detection is by UV absorbance at 225 nm or fluorescence with excitation at 225 nm and emission at 290 nm. Fluorescence detection is advantageous for trace analysis.

Alkyl sulfates Alkyl sulfates with chain lengths in the surfactant range (C_{10} and higher) are readily separated according to increasing alkyl chain length in a reversed-phase system with methanol/water mobile phase containing a salt such as sodium perchlorate. The pH is often adjusted to 2.5 or 3.0. Gradient programming is impractical if detection is by direct low wavelength UV, differential refractive index (DRI) or conductivity. Gradients are successful with detection by indirect UV (typically, methylpyridinium chloride is added to the eluent) or evaporative light scattering (ELS). If anion exchange chromatography is used, elution is in order of decreasing alkyl chain length.

Alkanesulfonates These are generally separated with the same systems used for alkyl sulfates. In a mixture, the peaks of the alkyl sulfates and alkanesulfonates are interspersed, with the alkyl sulfates more strongly retained on reversed-phase column packings than alkanesulfonates of the same chain length. Separation from anionic surfactants of other types is usually straightforward. Interference from alkyl sulfates can be eliminated by subjecting the sample to acid hydrolysis to convert them to the corresponding alcohols and sulfuric acid; sulfonates are not affected by this treatment.

Ether sulfates Alkylphenol ether sulfates and alcohol ether sulfates can be resolved by reversed-phase chromatography with elution in the order of both increasing alkyl chain length and increasing (or decreasing) ethoxy chain length (**Figure 3**). An alkylamine ion-pairing agent may be added to increase retention time. Unsulfated alcohol or alkylphenol ethoxylate impurities elute first under paired-ion conditions. A single peak for easy quantification can sometimes be obtained by using a very short reversed-phase column and a step gradient.

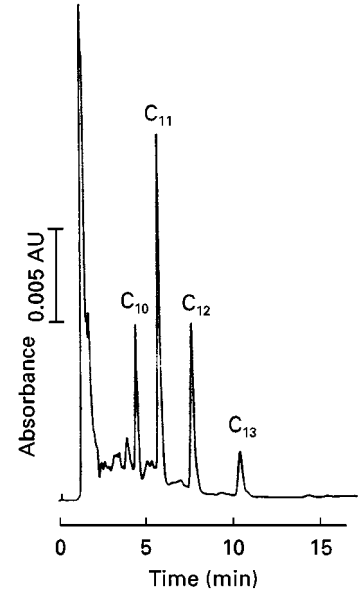


Figure 1 LAS isolated from river water and analysed isocratically using a C_4 reversed-phase column. Labels indicate alkyl chain length. Column: Wakosil 5C4, 4.6 × 150 mm. Mobile phase: 0.1 mol L^{-1} sodium perchlorate in 50 : 50 CH_3CN/H_2O. Detection: UV, 220 nm. (Reproduced with permission from Yokoyama Y and Sato H (1991) Reversed-phase HPLC determination of linear alkylbenzenesulphonates in river water by precolumn concentration. *Journal of Chromatography* 555: 155–162. Copyright (1991) Elsevier Science.)

Normal-phase systems are also used for analysis of ether sulfates, with stationary phases of bare silica or

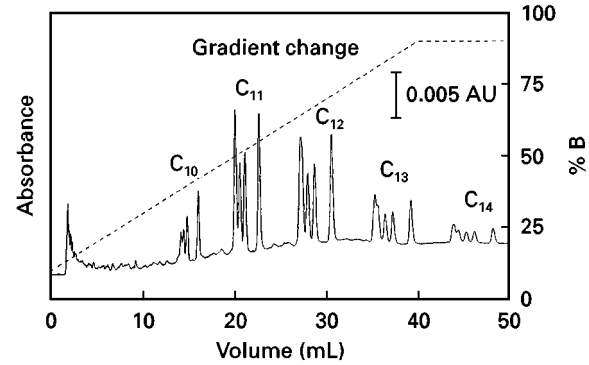


Figure 2 Chromatogram of commercial LAS mixture analysed using a reversed-phase column and gradient elution. Labels indicate groups of isomers for various alkyl chain lengths. Column: Zorbax ODS, 4.6 × 250 mm. Mobile phase: CH_3CN/H_2O gradient with increasing concentration of NaCl. Detection: UV, 225 nm. (Reproduced with permission from Chen S and Pietrzyk DJ (1994) Reversed-phase LC separation of linear alkylbenzenesulphonates. Effect of mobile phase ionic strength. *Journal of Chromatography A* 671: 73–82. Copyright (1994) Elsevier Science.)

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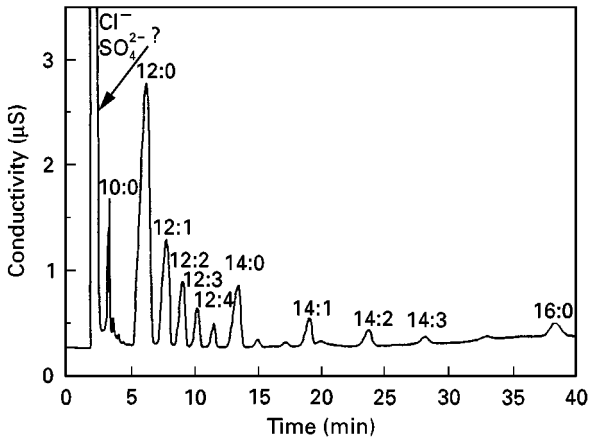

Figure 3 Chromatogram of a lauryl ether sulfate isolated from shampoo. Labels indicate alkyl chain length and number of moles of ethylene oxide. Column: Alltech Surfactant C_8, 4.6 × 250 mm. Mobile phase: MeOH/H_2O, 45 : 55, 0.00023 mol L^{-1} in NH_4OAc. Detection: conductivity. (Reproduced with permission from Stemp A, Boriraj VA, Walling P and Neill P (1995) Ion chromatographic characterization of ethoxylated anionic surfactants. *Journal of the American Oil Chemists' Society* 72: 17–21.)

amino- or cyanopropyl-silica. In this case, the nonionic material elutes first, followed by the anionic material, each in order of increasing ethoxylation. An ion-pairing agent such as cetyltrimethylammonium chloride may be added to give more rapid elution of anionic material. A relatively hydrophilic mobile phase is often used in conjunction with the ion-pairing agent.

α-Olefin sulfonates These compounds give complex chromatograms that reflect the complexity of their composition. The commercial product is formed of approximately equal portions of alkenesulfonates and hydroxyalkane sulfonates, each carrying the chain length distribution of the alkene feedstock. Disulfonates may also be present. α-Olefin sulfonates are analysed by reversed-phase LC with methanol/water and added salt. DRI or low wavelength UV detection is suitable. Elution is in order of increasing chain length, with hydroxyalkanesulfonates eluting prior to the corresponding alkenesulfonates and with all disulfonates eluting prior to all monosulfonates (**Figure 4**). Complete resolution is not obtained if the starting α-olefin was a mixture of many chain lengths, as is usually the case with commercial products.

Petroleum sulfonates and alkylnaphthalenesulfonates These are frequently separated on anion exchange packings with elution according to increasing degree of sulfonation. Reversed-phase systems have also been used. Resolution by alkyl chain length is sometimes attained, but, more often, the practitioners are content with a single peak for the active agent.

Ether carboxylates Only reversed-phase systems have been demonstrated for separation of these products, generally with acetonitrile/water mobile phase. Elution is always according to increasing chain length of the alkyl or alkylphenol moiety. Depending on the system, there may be an overtone of separation according to increasing or decreasing ethoxy chain length. As with ether sulfates, separation from nonionic impurities is straightforward. Alkylphenolether carboxylates are easily detected in the UV (225 or 254 nm), while the alkylether carboxylates require low wavelength UV, DRI or ELS detection.

Sulfosuccinate esters These are analysed most readily by reversed-phase LC in the presence of an ion-pairing agent. If not monodisperse as to alkyl chain length, they are eluted in order of increasing alkyl length. Separation from other anionic surfactants can usually also be accomplished by reversed-phase chromatography.

α-Sulfofatty acid methyl esters These also are easily separated according to alkyl chain length by reversed-phase methods. Ion-pairing agents are rarely used.

Soap Fatty acids are separated according to increasing alkyl chain length on a C_{18} column with methanol/water mobile phase and refractive index

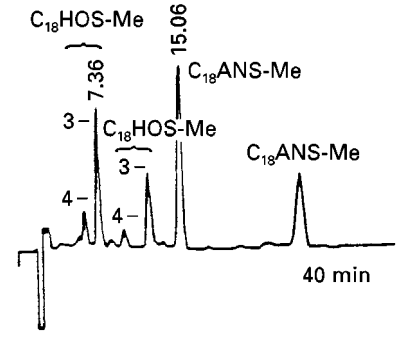

Figure 4 Chromatogram of α-olefin sulfonate after hydrogenation and formation of methyl esters. Peak identification: 4- and 3-hydroxyhexadecylsulfonate, methyl ester; 4- and 3-hydroxyoctadecylsulfonate, methyl ester; hexadecylsulfonate, methyl ester; octadecylsulfonate, methyl ester. Column: Inertsil C_{18}, 4.6 × 250 mm. Mobile phase: MeOH/H_2O, 85 : 15. Detection: refractive index. (Reproduced with permission from Matsutani S and Endo Y (1991) Separation and determination of sulfonate type anionic surfactants including 2-sulfonatofatty acid methyl ester by methyl ester derivatization and HPLC analysis. *Yukagaku* 40: 566–573.)

detection. Ionic strength and pH must be controlled. Analysis is either at low pH without an ion-pairing agent or at high pH with ion-pairing. It should be noted that most practitioners prefer GC for analysis of fatty acids (as methyl esters).

Cationic Surfactants

LC is the most generally useful method for determination of cationic surfactants. All commercial cationic surfactants are salts of quaternary amines (quats). Most of these, like the long-chain alkyltrimethylammonium salts, have good water solubility and are readily analysed by reversed-phase LC. Control of pH and ionic strength is necessary and inverse spectrophotometric detection gives the best results for quats without an aryl moiety; toluenesulfonate or xylenesulfonate are used as counterions for detection. Retention times are influenced by the hydrophobicity of the counterion. Conductivity detection is also applicable, especially if ion chromatography instrumentation is used with a nonpolar stationary phase (this configuration is sometimes called 'mobile-phase ion chromatography'). Of course, UV detection can be used for compounds with pyridyl or benzyl substituents. Since quats exhibit long retention times on C_{18} stationary phases, reversed-phase LC is most often performed on cyano columns, usually with methanol/water or acetonitrile/water mobile phase.

Quats are sometimes analysed using cation exchange packings. While the separating ability of the ion exchange systems is not as great as that attained with normal- or reversed-phase systems, ion exchange is sometimes preferred for formulation analysis because interference is minimized in that only the cationic materials are seen.

The quats used as fabric softeners for household laundry contain two long alkyl chains and have poor water solubility. For reasons of solubility, these are most easily analysed by normal-phase chromatography. Bare silica stationary phases are never used, but rather cyanoamino, amino, DIOL or polyphenol phases. Chloroform/methanol mobile phases work well, usually with a little added acetic acid. Conductivity and ELS are suitable for detection.

Common fabric softener quats, including ester quats, can be characterized by normal-phase chromatography on a polyphenol column with a hexane/methanol/THF gradient and added trifluoroacetic acid. Elution is in order of decreasing alkyl length, with the quats well resolved from unquaternized amine impurities.

For trace analysis, detection is sometimes accomplished by paired-ion extraction of the HPLC effluent with a fluorescent anion, followed by phase separation and fluorescence detection.

Nonionic Surfactants

Ethoxylated nonionics are most easily characterized by normal-phase chromatography. This permits the separation of the compounds according to the length of the ethoxy chain, with the longer chain homologues eluting later. Amino-bonded stationary phases are often used along with the usual nonpolar mobile phases such as hexane.

Separation of homologues can also be accomplished by reversed-phase chromatography. Reversed-phase LC is usually applied to higher ethoxylates because normal-phase LC resolution deteriorates with higher molecular weight. Solvent systems of methanol/water or acetonitrile/water are usual. Order of elution can be according to increasing or decreasing order of ethoxylation, depending on the particular reversed-phase media and solvents used, the particular nonionic surfactant and whether it has been derivatized. The order of elution even depends on the molecular weight: elution is sometimes according to reverse order of ethoxylation for lower members of a series and according to increasing order of ethoxylation for higher members of the same series.

Reversed-phase HPLC is effective for separation of ethoxylated surfactants according to the identity or chain length of the hydrophobic moiety. Caution is required, since under various reversed-phase conditions separation according to degree of ethoxylation will also occur, as mentioned above. Unless MS detection is available, this two-dimensional separation makes quantification difficult, so the system is usually optimized to minimize the influence of hydrophile homogeneity. If MS detection is used, then the separation by hydrophobe is sufficient for complete characterization of the surfactant, with the MS detector giving the information on ethoxy homologue distribution. The sensitivity of the MS detector is not identical for all homologues. For precise work, calibration must be performed over the entire range of composition.

Size exclusion chromatography (SEC) is sometimes applied to the analysis of nonionic surfactants, particularly higher molecular weight surfactants like the ethylene oxide/propylene oxide (EO/PO) copolymers. Nonaqueous systems are most useful for this analysis for two reasons. First, formation of micelles is discouraged. Micelle formation is a function of concentration, so SEC can show different values for molecular weight depending on sample concentration. Second, aqueous SEC column packings often have a silica backbone. Polyethoxy compounds are strongly adsorbed to silica, resulting in mixed-mode separation rather than separation only according to molecular size.

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Polyethylene glycol (PEG) impurity is determined in most ethoxylated surfactants by reversed-phase separation with 95 : 5 methanol/water and DRI or ELS detection. PEG elutes as a single peak prior to the surfactants.

The refractive index of nonionic surfactants is a function of degree of ethoxylation. Thus, the response of a differential refractive index detector varies for homologues, with the variation being most significant at low degrees of ethoxylation.

Alcohol ethoxylates (AE) Commercial products are mixtures of homologues containing a distribution of alkyl chain length and ethoxy chain length. Conventional LC analysis fails to give a single peak for alcohol ethoxylate. Rather it yields a series of peaks more-or-less resolved corresponding to the alkyl or ethoxy distribution. This limitation is only overcome by using backflush techniques.

Derivatives may be formed to improve detectability of AE. Derivatization also influences retention time, so that a gradient system optimized for underivatized AE must be modified for chromatography of the derivatives. Typical derivatizing agents are phenyl isocyanate, naphthyl isocyanate and 3,5-dinitrobenzoyl chloride. Fluorescence detection is sometimes used in environmental analysis with fluorescent derivatizing agents such as 1- and 2-naphthoyl chloride and naphthyl isocyanate.

Normal-phase chromatography, preferably on aminopropyl- or cyanopropyl-bonded silica, will give the ethoxy distribution (**Figure 5**). Reversed-phase chromatography on C_{18} media serves to separate by alkyl chain length. In either case, solvent programming is usually required for complete resolution of a commercial product, so either an ELS detector is used or the surfactant is first derivatized to permit use of a UV detector. If reversed-phase solvents are not optimized, a separation by ethoxy chain length is superimposed on the separation by alkyl chain length.

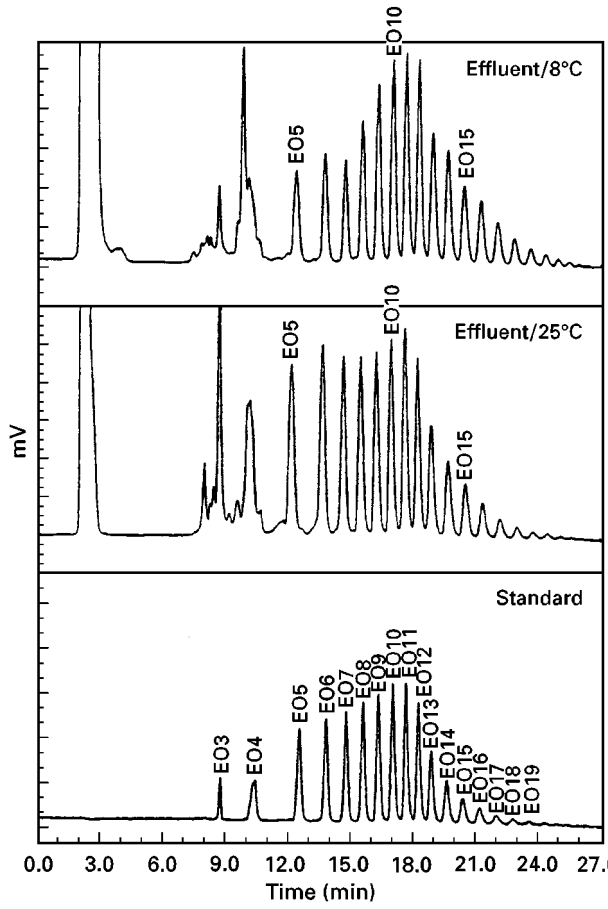

Figure 5 Chromatogram of C_{13} alcohol ethoxylate from a biotreatment study. Analysis using a CN normal phase column with gradient programming and evaporative light scattering detection. Labels indicate ethoxy chain length. Column: Rainin Microsorb CN, 4.6×250 mm, 45°C. Mobile phase: gradient, hexane/THF/(90 : 10 2-PrOH/H_2O); from 100 : 0 : 0 to 80 : 20 : 0 in 5 min, then to 52 : 30 : 18 in 15 min, then to 40 : 40 : 20 in 5 min. Detection: ELS (Reproduced with permission from Dubey ST, Kravetz L and Salanitro JP (1995) Analysis of nonionic surfactants in bench-scale biotreater samples. *Journal of the American Oil Chemists' Society* 72: 23–30.)

Alkylphenol ethoxylates (APE) Almost all commercial products are based upon a monodisperse hydrophobe, usually nonylphenol. Therefore, quantification is usually performed by reversed-phase chromatography on C_{18} media using a isocratic methanol/water or acetonitrile/water eluent and UV detection, resulting in a single peak. Octylphenol ethoxylates are easily separated from nonylphenol ethoxylates by such systems.

As with alcohol ethoxylates, separation by degree of ethoxylation is easily performed with any of the usual normal-phase stationary phases, with the cyano packings most popular. Amino and bare silica media are also used (**Figure 6**). Reversed-phase LC is also applied, especially for higher degrees of ethoxylation. UV detection (225 or 275 nm) is always used since it gives a uniform molar response to the homologues. For trace analysis, fluorescence detection is applicable since APEs have native fluorescence.

Ethoxylated acids These compounds can be considered as esters of PEG and fatty acids, with the commercial products also containing diester, residual fatty acid and free PEG. Reversed-phase chromatography with methanol/water separates the ethoxylated acid, PEG diester, free PEG and free fatty acid, and usually also serves to separate the compounds from other surfactants. As with other ethoxylates, normal-phase chromatography gives resolution by ethoxy chain length. SEC is often useful to resolve the

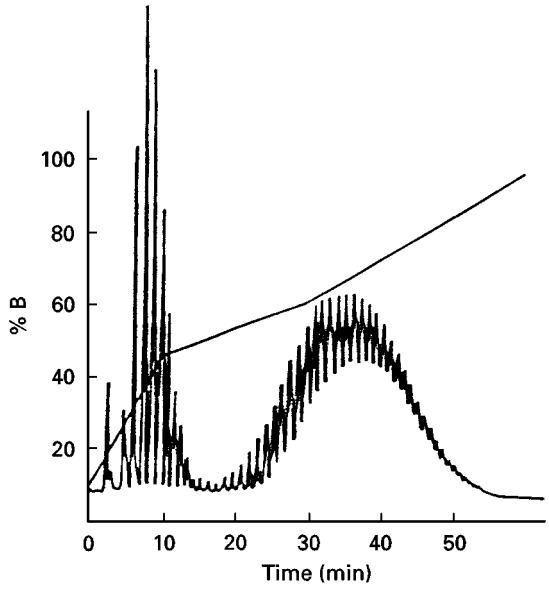

Figure 6 Chromatogram of a mixture of two commercial products, nominal 4-mole and 30-mole ethoxylates of nonylphenol, analysed by normal-phase HPLC. Column: Hewlett-Packard Si-100, 4.6 × 200 mm, 30°C. Mobile phase: gradient; A = 80/20 *n*-hexane/ethyl ether; B = 40 : 30 : 20 : 10 : 1 : 0.5 dioxane/ethyl ether/*n*-hexane/2-PrOH/H_2O/HOAc; 5 to 95% B in 45 min. Detection: UV, 280 nm. (Reproduced with permission from Anghel DF, Balcan M, Voicu A and Elian M (1994) *Journal of Chromatography A* 668: 375–383. Copyright (1994) Elsevier Science.)

mono- and diesters. DRI and ELS detectors are most applicable. Low wavelength UV detection must be used with caution because of the disproportionate response from unsaturated fatty acid moieties.

Esters Esters of fatty acids with glycerol and sugars are separated according to degree of acyl character by either normal-phase or reversed-phase chromatography. Reversed-phase elution is according to increasing acyl character, while normal-phase elution is in order of decreasing acyl character (i.e. according to both the chain length of the acyl groups and their number). Normal-phase LC is usually performed with a DIOL stationary phase and propanol/water mobile phases. The ELS detector is most applicable, although historically many applications have been developed using DRI or UV at wavelengths of 220 nm or less.

EO/PO block copolymers In the absence of interfering compounds, polymers of the poloxamer type can sometimes be determined by reversed-phase HPLC with methanol, but the most common separation technique is SEC. The copolymers useful for detergents and pharmaceuticals are higher in molecular weight than most other synthetic surfactants, so SEC can be used for both qualitative and quantitative analysis. If conventional LC is used, depending on the specific product, a reversed-phase system with acetonitrile/water can be optimized to be indifferent to EO chain length, separating the surfactant according to length of the PO chain. DRI detection is generally used for the block copolymers.

Alkanolamides These compounds, for example the C_{10}–C_{18} fatty acid monoethanolamides, are eluted according to increasing acyl chain length by reversed-phase chromatography with methanol/water solvents. These systems may also be used for formulation analysis. Detection is a challenge: DRI and low wavelength UV are most common, and ELS and nitrogen-specific detectors have been applied in more recent times. *N*-Methylglucosamides are analysed in the same way.

Alkyl polyglycosides Reversed-phase LC with methanol/water will separate these compounds, with elution according to increasing chain length of the acyl constituents. For compounds of the same acyl chain length, polyglycosides elute prior to monoglycosides. ELS detection is typically used.

Amphoteric Surfactants

Amphoteric surfactants are almost always separated on C_{18} columns with methanol/water mobile phase. The pH is often held as low as the column will tolerate and a salt such as sodium perchlorate is added. Under such conditions, the amphoteric surfactant behaves much like a cationic surfactant and the same detection methods are used as discussed above for cationics.

Betaines These compounds can be separated, with elution by increasing alkyl chain length by reversed-phase LC or by decreasing chain length using cation exchange chromatography. DRI detection is most often chosen, although low wavelength UV and ELS are sometimes applied.

Phosphatides These compounds must be discussed separately from other amphoterics. They are constituents of the natural surfactant, lecithin, but they also have great biochemical importance. Normal-phase LC serves to separate the main constituents of commercial lecithin: phosphatidylethanolamine, phosphatidylcholine, phosphatidylinositol, phosphatidylserine and phosphatidic acid. (Each of these consists of a number of individual compounds containing various acyl groups.) The normal-phase separation is traditionally performed on a bare silica column with low wavelength UV detection. Since it is mainly double

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bonds that give the detector response, and since each of the individual components contains acyl chains of varying unsaturation, quantification by UV is only approximate. The ELS detector is rapidly becoming standard for this analysis. Since this detector is tolerant of solvent gradients, other normal-phase columns, notably the DIOL column, may be used instead of bare silica. These give better reproducibility but do not have sufficient resolving power for lecithin analysis in the absence of gradient programming.

Separation by acyl chain length is accomplished by reversed-phase LC of fractions separated by the normal-phase methods. LC–MS is an obvious way to simplify the characterization of unknowns. Precise phosphatide analysis is very much an activity of specialists and the field is advancing rapidly.

Conclusions

LC is the only practical method to characterize many surfactants according to their oligomer or homologue distribution. It is also the best way to determine quantitatively many surfactants, particularly ionic surfactants.

However, in spite of improvements in instrumentation and in stationary phases, LC is not easy. It demands more time and training of the operator than most analytical techniques. Preliminary sample preparation is very often necessary for mixtures and environmental samples, making an LC analysis an expensive analysis.

Continued development in the areas of detection (especially in element-selective detectors, detectors specific for chemical functionality, and LC–MS interfaces) will make LC even more useful in the future. For example, the ELS detector, even though suffering from problems in linearity in its present incarnation, has already greatly expanded the utility of LC for analysis of lecithin and ethoxylates.

See also: **II/Chromatography: Liquid:** Mechanisms: Ion Chromatography; Ion Pair Liquid Chromatography; Mechanisms: Reversed Phases. **Extraction:** Solid-Phase Extraction.

Further Reading

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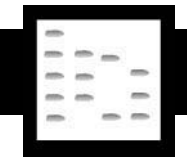
SYNTHETIC POLYMERS



Gas Chromatography

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Introduction

Successful gas chromatography (GC) requires that the sample be volatile at the operating temperature. The majority of synthetic polymers are of substantial molecular weight, i.e. in excess of 20 kDa, and not amenable to direct chromatographic examination.